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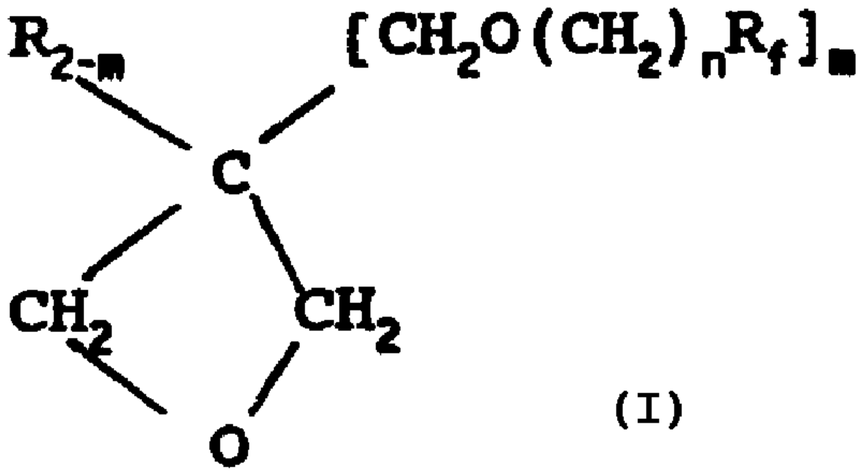
(54) Title: PREPARATION AND POLYMERIZATION OF PERFLUOROALKOXY ALKYLENE OXIDES TO PREPARE HYDROPHOBIC POLYETHERS



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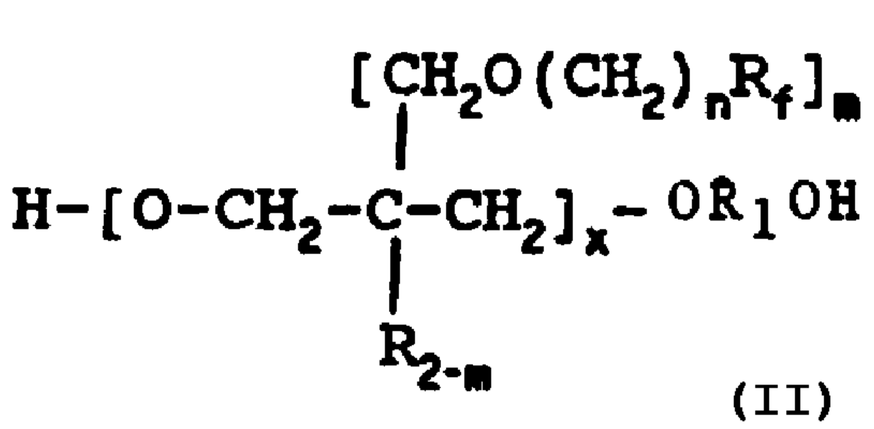
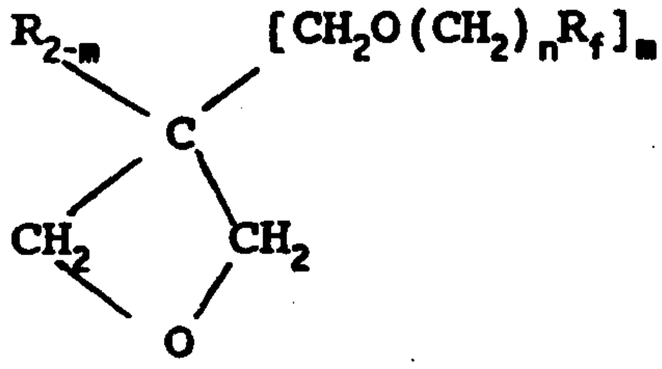


(II)

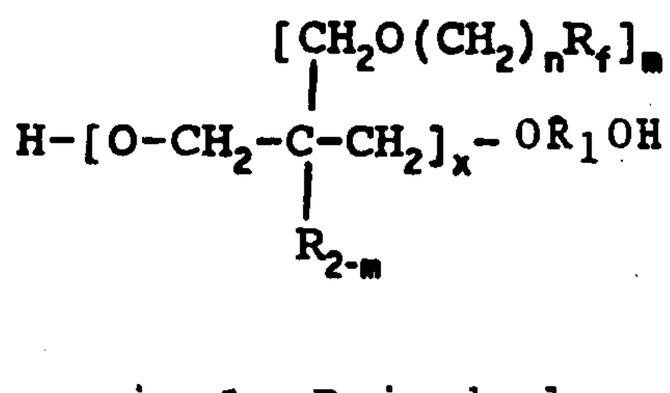
(57) Abrégé/Abstract:
Oxetane monomers having perfluorinated alkoxy side chains; a method for their preparation; a method for their polymerization; and the resultant prepolymers are disclosed. The monomers have the formula: (see formula I) wherein n is 1 to 5, m is 1, R is hydrogen or alkyl having from 1 to 4 carbons; and R_f is linear or branched chain perfluorinated alkyl having from 1 to 20 carbons, or an oxaperfluorinated polyether, having from 4 to about 60 carbons, and the resultant prepolymers have the formula: (see formula II) wherein n is 1 to 5, m is 1, R is hydrogen or alkyl having from 1 to 4 carbons, R_1 is alkylene or isoalkylene having 2 to about 5 carbons, R_f is linear or branched chain perfluorinated alkyl having from 1 to 20 carbons, or an oxa-perfluorinated polyether, having from 4 to about 60 carbons; and x is 2 to about 250. The monomers are prepared by the reaction of fluorinated alkoxides with aryl sulfonate derivatives of 3-hydroxyalkyl oxetanes, e.g., the p-toluene sulfonate derivative of 3-hydroxymethyl-3-methyl oxetane or of 3,3-bis(hydroxymethyl)oxetane. A high yield of the oxetanes having pendant perfluorinated alkoxy side chains is obtained. The fluorinated alkoxy oxetane monomers of this invention can be readily polymerized in the presence of Lewis acid catalysts and polyhydroxy aliphatics to obtain high yields of hydroxyterminated prepolymers having molecular weights from 1,000 to about 30,000, and a polymer backbone resulting from the opening of the oxetane ring.

ABSTRACT

Oxetane monomers having perfluorinated alkoxy side chains; a method for their preparation; a method for their polymerization; and the resultant prepolymers are disclosed. The monomers have the formula:



wherein n is 1 to 5, m is 1, R is hydrogen or alkyl having from 1 to 4 carbons; and R_f is linear or branched chain perfluorinated alkyl having from 1 to 20 carbons, or an oxa-perfluorinated polyether, having from 4 to about 60 carbons, and the resultant prepolymers have the formula:



wherein n is 1 to 5, m is 1, R is hydrogen or alkyl having from 1 to 4 carbons, R_1 is alkylene or isoalkylene having 2 to about 5 carbons, R_f is linear or branched chain perfluorinated alkyl having from 1 to 20 carbons, or an oxa-perfluorinated polyether, having from 4 to about 60 carbons; and x is 2 to about 250. The monomers are prepared by the reaction of fluorinated alkoxides with aryl sulfonate derivatives of 3-hydroxyalkyl oxetanes, e.g., the p-toluene sulfonate derivative of 3-hydroxymethyl-3-methyl oxetane or of 3,3-bis(hydroxymethyl)oxetane. A high yield of the oxetanes having pendant perfluorinated alkoxy side chains is obtained. The fluorinated alkoxy oxetane monomers of this invention can be readily polymerized in the presence of Lewis acid catalysts and polyhydroxy aliphatics to obtain high yields of hydroxyterminated prepolymers having molecular weights from 1,000 to about 30,000, and a polymer backbone resulting from the opening of the oxetane ring.

PREPARATION AND POLYMERIZATION OF PERFLUOROALKOXY ALKYLENE OXIDES TO PREPARE HYDROPHOBIC POLYETHERS

BACKGROUND OF THE INVENTION

Field Of Invention

This invention relates to oxetane monomers having pendant perfluoroalkoxy groups, to a method for their preparation and a method for their polymerization, and to the hydroxy-terminated prepolymers so prepared. The prepolymers have a polyether backbone and are useful for the preparation of resins and coatings having hydrophobic properties, low di-electric constants and low refractive indices.

Brief Statement Of The Prior Art

It is known that oxetane can be substituted in the 3-position with methyl groups containing energetic functional groups such as nitrato, azide, nitro and difluoroamino. The polymerization of these substituted oxetanes in the presence of polyhydroxy aliphatic compounds produces hydroxy-terminated polymers having a polyether backbone with pendant energetic groups. These polymers may then be cured with isocyanates, forming high molecular weight polymers which are useful as binders in propellent applications as described in U.S. Patents 4,393,199; 4,483,978; 4,707,540; and 4,764,586.

It is desirable to incorporate fluorine in the polyether polymers, however, the incorporation of high percentages of fluorine in an ether backbone of a polymer causes thermal and chemical instability, resulting in the generation of fluoride ion or hydrogen fluoride. When the fluorine is incorporated in polymers which lack an ether linkage, the resulting materials have high glass transition temperatures which limit the usefulness and applications of the resulting polymers.

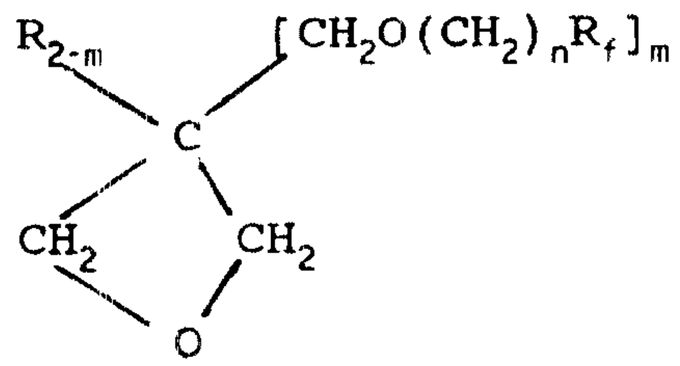
BRIEF DESCRIPTION OF THE INVENTION

This invention comprises oxetane monomers having alkoxy side chains with a fully fluorinated omega carbon, preferably perfluorinated alkoxy side chains, a method for their preparation, a method for their polymerization and to the resultant prepolymers. The monomers are prepared by the reaction of the corresponding fluorinated alkoxides with aryl sulfonate or halogenated derivatives of 3-hydroxyalkyl oxetanes. An example of the latter is the p-toluene sulfonate derivative of 3-hydroxymethyl-3-methyl oxetane or the derivative of 3,3-bis(hydroxymethyl)-oxetane. A high yield of the oxetanes having pendant perfluorinated alkoxy side chains is obtained.

The fluorinated alkoxy oxetane monomers of this invention can be readily polymerized in the presence of Lewis acid catalysts to obtain high yields of hydroxy-terminated prepolymers having molecular weights from 1,000 to about 30,000, and a polyether backbone resulting from the opening of the oxetane ring. These prepolymers are useful as hydrophobic, non-stick coatings and as precusors for binders for propellants.

DESCRIPTION OF PREFERRED EMBODIMENT

This invention comprises the following oxetane derivatives, a method for their preparation, a method for their polymerization and the resulting prepolymers:



wherein:

n is 1 to 5;

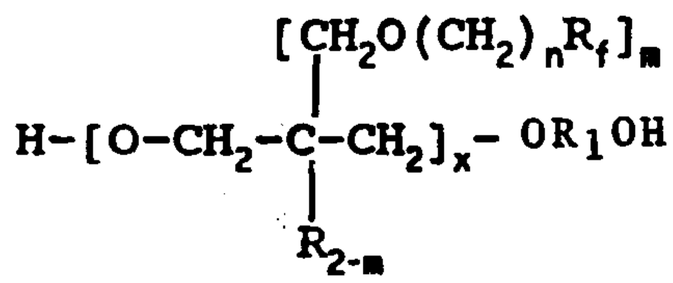
m is 1;

R is hydrogen or alkyl having from 1 to 4 carbons; and

R_f is linear or branched chain perfluoro-

alkyl having from 1 to 20 carbons, a linear or branched perfluorinated isoalkyl having from 1 to 20 carbons, or an oxa-perfluorinated polyether, having from 4 to about 60 carbons.

The invention also comprises the polymerization of the monomer and the resultant hydroxy-terminated prepolymers having the structure indicated below:



wherein:

wherein n is 1 to 5;

m is 1;

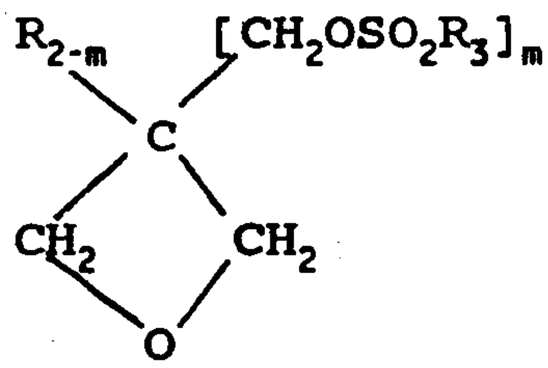
R is hydrogen or alkyl having from 1 to 4 carbons;

R_1 is alkylene or isoalkylene having 2 to about 5 carbons;

R_f is linear or branched chain perfluorinated alkyl having from 1 to 20 carbons, or an oxa-perfluorinated polyether having from 4 to about 60 carbons; and

x is 2 to about 250.

The oxetane derivatives are obtained by reaction of aryl sulfonate derivatives of hydroxyalkyl oxetanes with fluorinated alkoxides. The aryl sulfonate derivatives of the hydroxyalkyl oxetanes have the general formula:



wherein:

m is 1;

R is hydrogen or alkyl having from 1 to 4 carbons; and

wherein:

m is 1;

R is hydrogen or alkyl having from 1 to 4 carbons; and

R_3 is monocyclic aryl having from C_6 to C_{10} carbons, e.g., benzyl, tolyl, xylyl, mesityl.

The preferred sulfonates are toluene sulfonates, e.g. p-toluene sulfonate derivatives of oxetane.

The fluorinated alkoxides are obtained by the reaction of fluorinated alcohols with sodium hydride in a suitable solvent such as dimethylformamide. The fluorinated alcohols which can be used have the general formula:

$$R_f(CH_2)_nOH$$

wherein:

n is 1 to 5,

R_f is linear or branched chain perfluorinated alkyl having from 1 to 20 carbons, or an oxa-perfluorinated polyether, having from 4 to about 60 carbons.

Examples of suitable fluorinated alcohols are: trifluoro-ethanol, heptafluorobutanol, pentadecafluorooctanol, tridecafluorooctanol, etc. Other useful alcohols include fluorinated alcohols having other halogens, in the omega position, e.g., omega-halo perfluorinated alcohols of the following formulas:

1. $HOCH_2(CF_2)_nCF_2X$ and
2. $HOCH_2(CF_2CF)_n\underset{\displaystyle CF_3}{\underset{|}{C}}F_2X$

wherein:

X is halo, e.g., bromo, iodo, chloro or fluoro; and

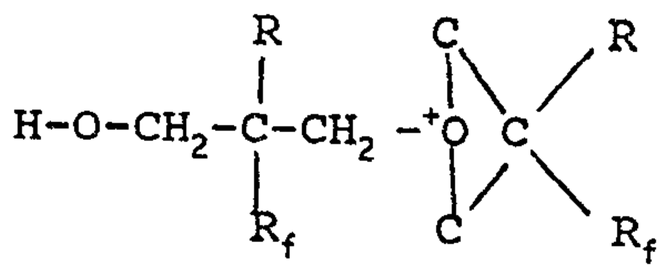
n is 2 to about 20; and

3. $HOCH_2(OCF_2CF_2)_nF$, and
4. $HOCH_2(OCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}F)_nF$

wherein n is 2 to about 20.

The fluorinated alkoxy oxetane monomers readily polymerize in the presence of a Lewis acid catalyst and a polyhydroxy aliphatic compound as a polymerization initiator. In the

presence of a Lewis acid, the alcohol releases a proton which initiates the ring opening polymerization of the oxetane which propagates through the formation of the following intermediate:



Suitable catalysts are Lewis acids, i.e., compounds capable of accepting a pair of electrons, examples of which include: complexes of boron trifluoride, phosphorus pentafluoride, antimony pentafluoride, zinc chloride, aluminum bromide, etc.

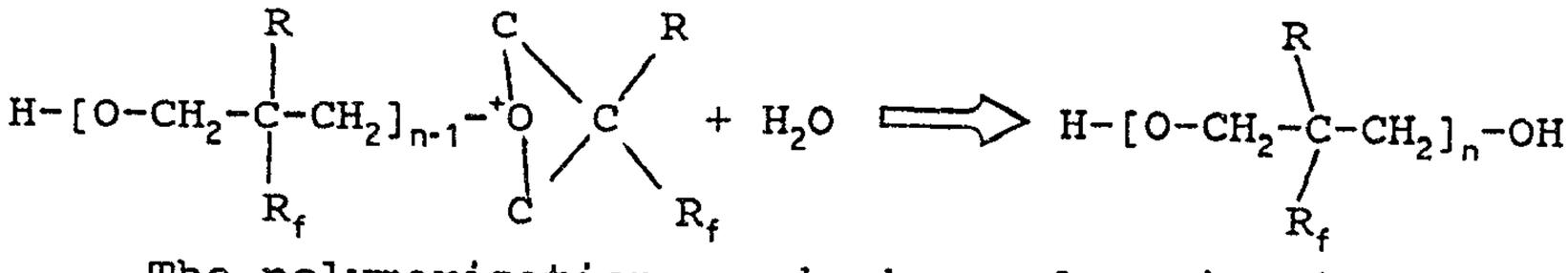
Suitable initiators are polyhydroxy aliphatic compounds such as alkyl and isoalkyl polyols having from 2 to about 5 carbons and from 2 to 4 hydroxyls, e.g., ethylene glycol, butane-1,4-diol, propylene glycol, isobutane-1,3-diol, pentane-1,5-diol, pentaerythritol, etc.

The polymerization is conducted in the presence of a suitable inert solvent, preferably a halogenated C_1 to C_5 hydrocarbon, e.g., methylene chloride, methylene bromide, ethylene dichloride, ethylene dibromide, propylene dichloride, Freons, fluorinated solvents, etc.

The catalyst and initiator are preferably mixed in the solvent prior to the addition of the oxetane monomer. An example of a preferred catalyst, initiator and solvent combination is the boron trifluoride etherate, or boron trifluoride tetrahydrofuranate, and butane-1,4-diol in methylene chloride.

To this mixture the monomer is added and solution polymerization is practiced at solution concentrations from 5 to 75 weight percent. In the polymerization, the concentration of the catalyst and the proportions of the initiator, e.g., butane-1,4-diol, can be varied to control the molecular weight of the polymer, with higher proportions of initiator resulting in lower molecular weight of the prepolymer product. Useful proportions of boron trifluoride catalyst to initiator can be from about 100:1 to about 1:2.

The polymerization terminates with the formation of the hydroxy-terminated polymer according to the following mechanism:



The polymerization can be homopolymerization or copolymerization in which a mixture of two or more of the afore-described oxetane monomers is added to the polymerization zone. A particularly useful copolymerization is block polymerization in which the comonomers are sequentially added in selected proportions to obtain block copolymers of controlled block sizes and properties.

To prepare prepolymers with the optimum coating properties, the oxetane monomer should have a 3-substituent in which the R_f group has its omega carbon fully fluorinated. One of the main applications of the hydroxy-terminated prepolymers of this invention is in the development of hydrophobic, non-stick coatings. The most important criteria in the development of these coatings is the minimization of the free surface energy of the coating, which is a measure of the wettability of the coating and defines critical properties, such its hydrophobicity and adhesive characteristics. Terminal carbons which contain hydrogen, e.g., $-CF_2H$ or $-CFH_2$ or $-CH_3$, have significantly greater surface energies (15-39 dynes/cm) than those with fully halogenated groups, e.g., those with $-CF_3$ groups, which have surface energies of about 6 dynes/cm.

Most preferably, the 3-substituent (R_f) is perfluoroalkyl. The perfluoroalkyl group is an extremely strong electron withdrawing group and its presence changes the electronic and steric properties, of the oxetane monomers. This affects the ease of their polymerization and the functionality, molecular weight, and structure, i.e., cyclic or linear, of the polymer. The most useful hydroxy-terminated prepolymers with fluorinated side chains

are those which are well defined and which have a functionality of at least 2. Presence of non-functional or mono-functional materials in the prepolymers results in coatings with poor mechanical and surface properties.

Cyclic groups, mainly cyclic tetramers and trimers, in the polymer are non-functional and reduce the usefulness of the prepolymers. Other non-functional groups can be formed by counter-ion terminations, such as diethyl ether and fluoride ion terminations. In addition to the role of the fluoroalkyl substituent on the oxetane on its reactivity, other factors thus control the formation of non- and mono-functional materials, such as the monomer/initiator ratio, ratio of alcohol to Lewis acid, type of Lewis acid, reaction temperature, solvent, and concentration.

Preferably, the hydroxyterminated prepolymer is one in which m is 1 and n is 2, and preferably R_f is tridecafluorooctyl. Also preferable is a hydroxyterminated prepolymer having a molecular weight from 1,000 to about 30,000, and a polymer backbone resulting from the opening of the oxetane ring of oxetane monomers substituted at the 3 carbon position with one to two perfluorinated alkoxide groups of the formula:

$$CH_2O(CH_2)_nR_f$$

wherein:

n is 1 or 2; and

R_f is linear or branched chain perfluorinated alkyl having from 1 to 20 carbons, a linear or branched perfluorinated isoalkyl having from 1 to 20 carbons, or an oxa-perfluorinated polyether, having from 4 to about 60 carbons.

In this case, n is preferably 2. R_f is preferably tridecafluorohexyl.

The preferred perfluorinated alkoxy oxetane monomer is one in which m is 1 and n is 2 and preferably R_f is tridecafluorohexyl.

It is also desired to use mono-3-substituted oxetanes, i.e., the value of "m" in the empirical formula is 1. These are desired, since homopolymerization of di-3-substituted oxetane monomers yields crystalline polymers. As an example, polymerization of 3,3-bis-(chloromethyl)oxetane yields a crystalline polymer that melts in the neighborhood of 220°C.

The hydroxyterminated prepolymers prepared from the preferred mono-3-substituted oxetane monomers are amorphous, low viscosity oils which are easy to process. The prepolymers are relatively pure, whereas those derived from di-3-substituted oxetane monomers contain large amounts of nonfunctional cyclic oligomers. Also, the desired surface properties of the prepolymer can be achieved with only one fluorinated substituent in the 3 position of the oxetane monomer, and a second fluorinated substituent does not significantly contribute to the surface properties.

In the following examples, the polymerization was practiced with boron trifluoride etherate, or boron trifluoride tetrahydrofuranate, in butane-1,4-diol. The initiator was prepared from commercial grade boron trifluoride etherate which was distilled prior to use. Similarly, the butane-1,4-diol was distilled from calcium

hydride and stored over a 4 Å molecular sieve prior to use.

The polymerizations were conducted in a 100 milliliter glass flask which was jacketed and equipped with a mechanical stirrer. NMR analysis of products was performed on a Bruker MSL-300 spectrometer at 300 MHZ in deutrochloroform solution with proton and carbon shifts in ppm relative to tetramethylsilane and fluorine shifts relative to fluorotrichloromethane. The infrared analysis was done by diffuse reflectance on a Nicolet SX-5 spectro meter on KBr. The thermal analysis was performed on a Dupont DSC 9100 analyzer. Weight average molecular weights were determined using a Waters gelpermeation chromatograph equipped with four columns (100 Å,500 Å, 10^3 Å and 10^4 Å), a differential refractive index detector and a Data Module 730.

EXAMPLE 1

PREPARATION OF 3-(2,2,2-TRIFLUOROETHOXYMETHYL)-3-METHYLOXETANE.

A dispersion of 50 weight percent (2.8 grams, 58.3 mmol) sodium hydride in mineral oil, was washed twice with hexanes and suspended in 35 milliliters of dimethyl formamide. Then, 5.2 grams (52 mmol) of trifluoroethanol was added and the mixture was stirred for 45 minutes. A solution of 10.0 grams (39 mmol) of 3-hydroxymethyl-3-methyloxetane p-toluenesulfonate in 15 milliliters of dimethyl formamide was added and the mixture was heated at 75-85°C for 20 hours, when ^{1}H NMR analysis of an aliquot sample showed that the starting sulfonate had been consumed.

The mixture was poured into 100 milliliters of ice water and extracted with 2 volumes of methylene chloride. The combined organic extracts were washed twice with water, twice with 2 weight percent aqueous hydrochloric acid, brine, dried over magnesium sulfate, and evaporated to give 6.5 grams of 3-(2,2,2-trifluorethoxymethyl)-3-methyloxetane as an oil containing less than 1 weight percent dimethyl formamide. The yield of this product was 90 percent. The oil was distilled at 30°C and 0.2 millimeters mercury

pressure to give 4.3 grams of analytically pure product, corresponding to a 60 percent yield. The analyses of the product were as follows: IR (KBr) 2960-2880, 1360-1080, 990, 840 cm^{-1}; ^1H NMR 1.33 (s,2H), 3.86 (q, J=8.8 Hz, 2 H), 4.35 (d, J=5.6Hz, 2 H), 4.51 (d, J=5.6 Hz, 2 H); ^{13}C NMR 20.72, 39.74, 68.38 (q, J=40 Hz), 77.63, 79.41, 124 (q, J=272 Hz). The calculated elemental analysis for $C_7H_{11}F_3O_2$ is: C=45.65; H=6.02; F=30.95. The experimental analysis found: C=45.28; H=5.83; F=30.59.

EXAMPLE 2

PREPARATION OF 3,3-BIS-(2,2,2-TRIFLUOROETHOXYMETHYL)OXETANE

A 50 weight percent dispersion of sodium hydride in 18.4 grams (0.383 mol) of mineral oil, was washed twice with hexanes and was suspended in 200 milliliters of dimethyl formamide. Then, 38.3 grams (0.383 mol) trifluoroethanol was added dropwise over 45 minutes while hydrogen gas evolved. The mixture was stirred for 30 minutes and a solution of 30.0 grams (0.073 mol) of 3,3-bis(hydroxymethyl)oxetane di-p-toluenesulfonate in 50 milliliters of dimethyl formamide was added. The mixture was heated to 75°C for 64 hours when ^1H NMR analysis of an aliquot showed that the starting sulfonate had been consumed.

The mixture was poured into water and extracted with two volumes of methylene chloride. The combined organic extracts were washed with brine, 2 weight percent aqueous hydrochloric acid, water, dried over magnesium sulfate, and evaporated to give 17.5 grams of 3,3-bis(2,2,2-trifluoro-ethoxymethyl)oxetane as an oil containing less than 1 weight percent dimethyl formamide. The oil was purified by bulb-to-bulb distillation at 42-48°C and 10.1 millimeters mercury pressure to give 15.6 grams of analytically pure ether, corresponding to a 79 percent yield. The analyses of the product were as follows: IR (KBr) 2960-2800, 1360-1080, 995, 840 cm^{-1}; ^1H NMR 3.87 (s, 4 H), 3.87 (q, J=8.8 Hz, 4 H), 4.46 (s, 4 H); ^{13}C NMR 43.69, 68.62 (q, J = 35 Hz), 73.15,

75.59, 123.87 (q, J=275 Hz); ^{19}F-74.6 (s). The calculated elemental analysis for $C_9H_{12}F_6O_3$ is: C=38.31; H=4.29; and F=40.40. The experimental analyses found: C=38.30; H=4.30; and F= 40.19.

EXAMPLE 3

PREPARATION OF 3-(2,2,3,3,4,4,4-HEPTAFLUORO-BUTOXYMETHYL)-3-METHYLOXETANE

A 50 weight percent dispersion of sodium hydride 6.1 grams (127 mmol) in mineral oil, was washed twice with hexanes and was suspended in 60 milliliters of dimethyl formamide. Then 24.0 grams (120 mmol) of 2,2,3,3,4,4,4-heptafluorobutan-1-ol was added and the mixture was stirred for 45 minutes. A solution of 25.0 grams (97.5 mmol) of 3-hydroxymethylp-toluenesulfonate in 15 milliliters of dimethyl formamide was added and the mixture was heated at 75-85°C for 30 hours when ^{1}HNMR analysis of an aliquot showed that the starting sulfonate had been consumed.

The mixture was poured into 100 milliliters of ice/water and extracted with two volumes of methylene chloride. The combined organic extracts were washed twice with water, twice with 2 weight percent aqueous hydrochloric acid, brine, dried over magnesium sulfate, and evaporated to give 27.5 grams of 3-(2,2,3,3,4,4,4-heptafluorobutoxyethyl)-3-methyloxetane as an oil. The oil was distilled at 33°C and 0.2 millimeters mercury pressure to give 12.2 grams of analytically pure ether, corresponding to a 44 percent yield. The experimental analyses were: IR (KBr) 2960-2880, 1280-1030, 995, 840 cm^{-1}, ^1H NMR 1.31 (s, 3 H), 3,67 (s 2 H), 3.99 (t, J=13.3 Hz 2 H) 4.34 (d. J=5.7 Hz 2 H) 4.50 (5.7 Hz, 2 H); ^{13}C NMR 20.242 (q, J=125 Hz) 39.627 (s) 67.778 (3x3. J=145.1 Hz, J=26.1 Hz), 77.730 (t. J=142 Hz), 79.110 (t, J=150 Hz), 108.72 (3 x 4, J=264 Hz. J=36 Hz), 114.7 (3 x 3, J=256 Hz, J = 30 Hz), 117.58 (4 x 3, J=286.9 Hz, J=33.7 Hz); ^{19}F -81.4, -120.6, -128.1. The calculated elemental analysis for $C_9H_{11}F_7O_2$ is C=38.04; H=3.90; F=46.80. The experimental analyses found: C=38.03; H=3.65; and F=46.59.

EXAMPLE 4

POLYMERIZATION OF 3-(2,2,2-TRIFLUOROETHOXYMETHYL)-3-METHYLOXETANE.

A solution of 34.3 milligrams (0.38 mmol) of butane-1,4-diol and 109.7 milligrams (0.77 mmol) of boron trifluoride etherate in 4 grams of methylene chloride was stirred at ambient temperature for 15 minutes under nitrogen in a dry polymerization flask. The solution was cooled to 1.5°C and a solution of 1.20 grams (6.52 mmol) of 3-(2,2,2-trifluoroethoxymethyl)-3-methyloxetane in 1.3 grams of methylene chloride was added. The resultant solution was stirred for 5 hours at 1-2° C at which time ^{1}H NMR analysis of an aliquot indicated that the starting oxetane had been consumed. The solution was warmed to ambient temperature and quenched with water. The organic layer was washed with brine, 2 weight percent aqueous hydrochloric acid, and evaporated to give 1.053 grams of poly-3-(2,2,2-trifluoro-ethoxymethyl)-3-methyloxetane as an oil, corresponding to a 88 percent yield. The polymer analyses were: DSC Tg -45°C, decomposition temperature was greater than 200°C; GPC (THF) Molecular weight Mn 7376, Mw 7951, polydispersity 1.08, inherent viscosity 0.008; Molecular Weight by ^{1}H NMR 6300; ^{1}H NMR 0.95 (s, 3 H), 3.26 (m, 4 H), 3.52 (2, 2 H) 3.84 (q. 2 H); ^{13}C NMR 17.57, 42.09, 69.30 (q, J=33 Hz), 74.42, 75.90, 125.18 (q, J=280 Hz).

EXAMPLE 5

PREPARATION OF

POLY-BIS-[3-(2,2,2-TRIFLUOROETHOXYMETHYL)OXETANE]

A solution of 33.9 milligrams (0.378 mmol) of butane-1,4 diol and 106.3 milligrams (0.75 mmol) of boron trifluoride etherate in 3.8 grams of methylene chloride was stirred at ambient temperature for 15 minutes under nitrogen in a dry polymerization flask. The solution was cooled to 1.5°C and a solution of 1.88 grams (6.67 mmol) of bis-[3-2,2,2-trifluoroethoxy-methyl)]oxetane in 2.3 grams of methylene chloride was added. The resultant solution was stirred for 16 hours at 1-2° C at which time ^{1}H NMR analysis

of an aliquot indicated that the starting oxetane had been consumed.

The solution was warmed to ambient temperature and quenched with water. The organic layer washed with brine, 2 percent aqueous hydrochloric acid, and evaporated to give 1.62 grams of polybis-[3-(2,2,2-trifluoroethoxymethyl)-oxetane, corresponding to 85% yield. The prepolymer was a waxy solid. The polymer analyses were: DSC Tg 54.88° C., mp 80.96° C (26.35 Joules/gram), decomposition temperature was greater than 210° C; GPC (THF) Molecular weight Mn 5321, Mw 7804, polydispersity 1.47, inherent viscosity 0.008; ^{1}H NMR 1.60 (m), 2.46 (s), 3.36 (s. 4 H), 3.58 (s, 4 H), 3.79 (q, 4 H); ^{13}C NMR 45.49, 68.25 (q. J=33 Hz), 69.20. 70.97. 123.81 (q, J=280 Hz).

EXAMPLE 6

PREPARATION OF POLY-3-(2,2,3,3,4,4,4-HEPTAFLUOROBUTOXYMETHYL)-3-METHYLOXETANE

A solution of 34.7 milligrams (0.38 mmol) of butane-1,4-diol and 109.7 milligrams (0.77 mmol) of boron trifluoride etherate in 3.4 grams of methylene chloride was stirred at ambient temperature for 15 minutes under nitrogen in a dry polymerization flask. The solution was cooled to 1.5° C and a solution of 2.00 grams (7.08 mmol) of 3-(2,2,3,3,4,4,4-hepta-fluorobutoxymethyl)-3-methyloxetane in 3.3 grams of methylene chloride was added. The resultant solution was stirred for 4 hours at 1.2° C; at which time ^{1}H NMR analysis of an aliquot indicated that the starting oxetane had been consumed.

The solution was warmed to ambient temperature and quenched with water. The organic layer washed with brine, 2 percent aqueous hydrochloric acid, and evaporated to give 1.65 grams of poly-3-(2,2,3,3,4,4,4-heptafluorobutoxy-methyl)-3-methyloxetane, corresponding to a 83% yield. The prepolymer was an oil and had the following analyses: GPC (THF) Molecular weight Mn 4066, Mw 5439, polydispersity 1.34, inherent viscosity 0.054. This oil was extracted with methanol and dried to give 1.46 grams of polymer,

corresponding to 72% yield, and has the following analyses: DSC Tg -45°C; GPC (THF) Molecular weight Mn 4417, Mw 5658, polydispersity 1.28 inherent viscosity 0.056. Molecular weight ^{1}H MMR 8718, ^{1}H NMR 0.93 (s, 3 H), 3.20 (m, 4 H), 3.48 (s, 2 H), 3.92 (q, J=13.6 Hz, 2 H); ^{13}C MMR 16.14, 40.57, 67.37 (t, J=Hz), 72.89, 74.76.

EXAMPLE 7

PREPARATION OF

3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-PENTADECAFLUORO-OCTYLOXYMETHY)-3-METHYLOXETANE

A dispersion of 50 weight percent sodium hydride (4.0 g, 83 mmol) in mineral oil was washed with hexanes and suspended in 200 milliliters of dimethylformamide. A solution of 30 grams of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctan-1-ol (75 mmol) in 50 milliliters of dimethylformamide was added over a period of 3 hours, and the resulting mixture was stirred at room temperature for one hour. Next, a solution of 9.3 grams (77 mmol) of 3-chloromethyl-3-methyloxetane in 20 milliliters of dimethylformamide was added and the resulting mixture was heated at 75°C. for 16 hours. The mixture was cooled to room temperature and slowly poured into 1 liter of ice/water and extracted with two volumes of Freon 113. The combined organic extracts were washed twice with water, once with 2 weight percent aqueous hydrochloric acid and once with brine, dried over magnesium sulfate, filtered, and evaporated to give 32 grams of crude product. The crude product was distilled under reduced pressure to give 26.5 grams (73%) of analytically pure 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8- pentadecafluorooctoxymethy)-3-methyloxetane, an oil with a boiling point 68 to 70°C./1.6 mm-Hg. The experimental analyses were: ^{1}H NMR ($CDCl_3$/Freon 113) δ 4.49 and 4.37 (AB, J=5.5 Hz, 4 H), 4.00 (triplet, J=13.2 Hz, 2 H), 3.70 (singlet, 2 H), and 1.32 (singlet, 2 H); ^{13}C NMR δ 21.02, 40.33, 68.77 (triplet, J=146.2 Hz), 78.60, and 79.87; ^{19}F NMR δ -81.3 (3 F), -119.9 (2F), -122.6 (2 F), -123.3 (2 F), -123.5 (2 F), -123.9 (2 F) and -126.8 (2 F). The

elemental analysis was: Calculated for $C_{13}H_{11}F_{15}O_2$: C, 32.2; H, 2.3; F, 58.9. Found: C, 32.2; H, 2.2; F, 58.3.

EXAMPLE 8

PREPARATION OF

3-(3,3,4,4,5,5,6,6,7,7,8,8,8-TRIDECAFLUORO-OCTYLOXYMETHYL)-3-METHYLOXETANE

In a manner similar to that described above, 12.0 grams of 3-bromomethyl-3-methyloxetane (73 mmol) was reacted with 26.5 grams of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-1-ol (72.7 mmol) in 300 milliliters) dimethyl-formamide in the presence of 3.9 grams of a 50 weight percent dispersion of sodium hydride (81 mmol) in mineral oil at 85°C. for 24 hours to give 21.5 grams (70% yield) of 3-(3,3,4,4,5,5,6,6,7,7,8,8,8- tridecafluorooctyloxy-methyl)-3-methyloxetane; a colorless oil with a boiling point of 66-68°C./2-2.5 mm-Hg; ^1H NMR ($CDCl_3$) δ 4.50 and 4.36 (AB, J=5.5 Hz, 4 H), 3.78 (t, J=6.6 Hz, 2 H), 3.53 (s, 2 H), 2.42 (triplet of triplets, J=6.6 and 18 Hz, 2 H), and 1.31 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 79.89, 63.31, 39.9, 31.64 (t), and 21.1 (signals due to carbons bearing fluorines are not included due to the complex splitting patterns and overlap of signals); ^{19}F NMR δ -81.4 (3 F), -113.8 (2 F), -118.2 (2 F), -122.3 (2 F), -123.3 (2 F), -124.1 (2 F) and -126.7 (2 F). The elemental analysis was: Calculated for $C_{13}H_{13}F_{13}O_2$: C, 34.8; H, 2.9; F, 55.1. Found: C, 35.1; H, 3.0; F, 54.7.

EXAMPLE 9

PURIFICATION OF COMMERCIAL FLUOROALCOHOLS

Zonyl BA-L is a narrow distribution, oligomeric mixture of fluoroalcohols that is available from Dupont Chemicals in pilot plant quantities. Zonyl BA-L is a yellow liquid which by GLC is a mixture of the following oligomers: 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol (C8, 60%); 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecan-1-ol (C1O, 26%); 3,3,4,4,5,5,6,6,7,7,8,8, 9,9,10,10,11,11, 12,12,12-heneicosafluorododecanol (C12, 6%); and various unidentified high boiling compounds (8%). Zonyl BA-L was

washed with equal volumes of 10 weight percent aqueous sodium thiosulfate, 10 weight percent aqueous sodium bicarbonate (to remove HF), water, and brine, dried, filtered, and distilled under reduced pressure (3 mm-Hg) at 50-100°C. to give a mixture of 69% C8, 26% C10 and 5% C12 in 83% yield.

EXAMPLE 10

PREPARATION OF A MIXTURE OF 3,3,4,4,5,5,6,6,7,7,8,8,8-TRIDECAFLUOROOCTYLOXYMETHYL-, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-HEPTADECAFLUORODECYLOXYMETHYL-, AND 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-HENEICOSAFLUORODODECYLOXYMETHYL-3-METHYLOXETANE

In a manner similar to that described above, a mixture of 69% C8, 26% C10 and 5% C12 fluoroalcohols (51.6 grams, 129 mmol) was reacted with 27 grams of 3-iodomethyl-3-methyloxetane (127 mmol) in 500 milliliters of dimethylformamide at 85°C. for 18 hours to give 60 grams of crude product. The crude product was fractionally distilled through a 6" Vigerux column to yield the following fractions: Fraction #1 (4.8 grams) was collected between 25°C. and 45°C. at 3.5-2.9 mm-Hg, and was a mixture of unreacted fluoroalcohols. Fraction #2 (2.8 grams) was collected at 45-71°C./0.7-3.0 mm-Hg, and was a mixture of unreacted fluoroalcohols and fluorinated oxetane monomers. The final fraction (49 grams, 80%), boiling at 70-85°C./0.7-0.9 mm-Hg, was a mixture of 73% 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxymethyl- 3-methyloxetane (C8-oxetane) , 24% 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyloxymethyl-3-methyloxetane (C10-oxetane), and 3% 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafluorododecyl-oxymethyl-3-methyloxetane (C12-oxetane), a colorless oil with a boiling point of 70-85°C./0.7-0.9 mm-Hg; ^{1}H NMR ($CDCl_3$) δ 4.50 and 4.35 (AB, J=5.9 Hz, 4 H), 3.78 (t, J=6.6 Hz, 2 H), 3.53 (s, 2 H), 2.42 (tt, J=6.6 and 17.6 Hz, 2 H), and 1.31 (s, 3 H); ^{13}C NMR δ

21.3, 31.86 (t, J=130.1 Hz), 40.2, 63.6, 76.8, and 80.2 (signals for carbons bearing fluorine are not included due to complex splitting patterns and overlap of signals); ^{19}F NMR δ -81.5, -113.8, -122.3, -123.3, -124.1, -124.5, -125.8, and -126.7.

EXAMPLE 11

PREPARATION OF 3,3-BIS(2,2,3,3,4,4,4-HEPTAFLUOROBUTOXY-METHYL)OXETANE

In a manner similar to that described above, 155 grams of 3,3-bis(chloromethyl)oxetane (1 mole) was reacted with 402 grams of 2,2,3,3,4,4,4-heptafluorobutan-1-ol (2.01 moles) in two liters of dimethylformamide in the presence of 100 grams of a 50 weight percent dispersion of sodium hydride in mineral oil, (2.3 moles) at 85°C. for 16 hours to give 340 grams (70% yield) of 3,3-bis(2,2,3,3,4,4,4-heptafluorobutoxymethyl)oxetane, a clear colorless liquid. Glc analysis revealed the purity of this material to be in excess of 99%, with a boiling point of 70-72°C./1.0-1.3 mm-Hg; ^1H NMR ($CDCl_3$) δ 4.44 (s, 4 H), 3.97 (t, J=13.2 Hz, 4 H), 3.86 (s, 4 H); ^{13}C NMR δ 43.9, 68.1 (t), 73.5, and 75.6 (signals from carbons bearing fluorine are not included due to the complex splitting patterns and overlap of signals); ^{19}F NMR δ -81.6 (3 F), -121.0 (2 F) and -128.3 (2 F). The elemental analysis was: Calculated for $C_{13}H_{12}F_{14}O_3$: C, 32.4; H, 2.5. Found: C, 32.3; H, 2.3.

EXAMPLE 12

PREPARATION OF 3,3-BIS(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-PENTADECA-FLUOROOCTYLOXYMETHYL)OXETANE

In a manner similar to that described above, 15.5 grams of 3,3-bis-(chloromethyl)oxetane (0.1 mole) was reacted with 84 grams of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadeca-fluorooctan-1-ol (0.21 moles) in 300 milliliters of dimethylformamide in the presence of 10.0 grams of a 50 weight percent dispersion of sodium hydride in mineral oil (0.23 moles) at 85°C. for 32 hours to give 58 grams (66%

yield) of 3,3-bis(2,2,3,3,4,4,4-heptadecafluorooctyl-oxymethyl)oxetane, a clear colorless liquid. An analytical sample was prepared by chromatographing the product on a silica gel column using methylene chloride as an eluent. The boiling point of the liquid was 130-35°C./1.0-1.2 mm-Hg. The analyses were: ^{1}H NMR ($CDCl_3$) δ 4.44 (s, 4 H), 3.96 (t, J=13.4 Hz, 4 H), 3.88 (s, 4 H); ^{13}C NMR δ 44.2, 68.7 (t), 73.9, and 76.5 (signals from carbons bearing fluorine are not included due to the complex splitting patterns and overlap of signals); ^{19}F NMR δ -81.5 (6 F), -119.7 (4 F), -121.5 (4 F), -122.6 (8 F), -123.3 (4 F), and -126.8 (4 F). The elemental analysis was: Calculated for $C_{21}H_{12}F_{30}O_3$: C, 28.6; H, 1.4; F, 64.6. Found: C, 28.2; H, 1.5.

EXAMPLE 13

COPOLYMERIZATION OF 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-PENTADECAFLUOROOCTYLOXYMETHYL)-3-METHYLOXETANE WITH 3-(2,2,2-TRIFLUOROETHOXYMETHYL)-3-METHYLOXETANE

A one-liter, three-necked, round-bottomed flask was fitted with a mechanical stirrer, nitrogen inlet/outlet tubes, a reflux condenser, a thermometer, and a constant addition funnel. The apparatus was dried with a heat gun, cooled under nitrogen to room temperature, and charged with a mixture of 0.914 grams of trimethylolpropane (6.52 mmol), 3.1 grams of boron trifluoride tetrahydrofuranate (22 mmol), 160 milliliters of 1,1,2-trichlorotrifluoroethane and 30 milliliters of anhydrous methylene chloride. The mixture was stirred at room temperature for 30 minutes, cooled to 10°C., and then treated, dropwise, with a solution of 106 grams of 3-(2,2,2-trifluoroethoxymethyl)-3-methyloxetane (576 mmol) and 94 grams of 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxymethy)-3-methyloxetane (195.2 mmol) in 40 milliliters of 1,1,2-trichloro-trifluoroethane. A mild exotherm was observed on addition of the monomer. The reaction temperature was maintained at 18°C. throughout the addition and the progress of the reaction was monitored by NMR analysis. The mixture was stirred at 18°C. for 2 hours and then at 25°C. for 4 hours

at which time NMR analysis of an aliquot indicated that 98 percent of the oxetane monomers were consumed. The reaction mixture was diluted with 50 milliliters of methylene chloride and 50 milliliters of 1,1,2-trichlorotrifluoroethane, and quenched with 50 milliliters of water. The organic layer was separated, washed with two equal volumes of water, and added dropwise to a 10 fold excess of methanol at room temperature. The precipitated oil was separated and redissolved in a 50:50 mixture of methylene chloride and 1,1,2-trichlorotrifluoroethane and transferred to a 500-milliliter, round-bottomed flask. The solvent was evaporated under reduced pressure and the resulting oil was dried at 85°C./2 mm-Hg for 16 hours to give 170 grams of a clear, colorless, viscous oil, corresponding to 85 percent yield. The NMR analyses of this material indicated it was a random copolymer of the above two monomers in a 74:26 ratio. The polymer analyses were: DSC, T_g=-40°C.; GPC (THF, polystyrene standard) Number Average Molecular weight was 6,178, Weight Average Molecular Weight was 7,286, Polydispersity was 1.18; Number average Molecular Weight by ^{1}H NMR was 7,040; Functionality was 3; Inherent viscosity was 0.065; ^{1}H NMR ($CDCl_3$) δ 0.94 (s, -C$\underline{H}_3$), 3.23 (m, backbone -C$\underline{H}_2$'S), 3.47 (s, -C$\underline{H}_2$O), 3.75 (q, J=8.6 Hz, -C$\underline{H}_2CF_3$) and 3.85 (t, J=13.5 Hz, -C$\underline{H}_2C_3F_7$); ^{1}H NMR ($CDCl_3$/Trifluoroacetic anhydride) δ 1.00 (s, -C$\underline{H}$3), 3.37 (m, backbone -C$\underline{H}_2$'s), 3.49 (s,-C$\underline{H}_2$O), 3.78 (q, J=8.6 Hz, -C$\underline{H}_2CF_3$), 3.96 (t, J=13.5 Hz, -C$\underline{H}_2C_3F_7$), and 4.30 (s, C$\underline{H}_2$OCOCF_3); ^{13}c NMR (CDC13) δ 17.1, 41.2, 41.3, 68.5 (t), 68.9 (q), 73.7, 75.3 and 75.5.

In a manner similar to that described above, random copolymers of above monomers in 50:50, 33:67, 25:75 and 10:90 ratios were also prepared. These copolymers were clear, colorless oils that were soluble in a solvent mixture of methylene chloride and 1,1,2-trichlorotrifluoroethane.

EXAMPLE 14

COPOLYMERIZATION OF 3-(2,2,2-TRIFLUOROETHOXYMETHYL)-3-METHYLOXETANE WITH 3-(2,2,3,3,4,4,4-HEPTAFLUOROBUTOXYMETHYL)-3-METHYLOXETANE

In a manner similar to that described in Example 13, a solution of 35 grams of 3-(2,2,2-trifluoro ethoxymethyl)-3-methyloxetane (190 mmol) and 183 grams of 3-(2,2,3,3,-4,4,4-heptafluorobutoxymethyl)-3-methyloxetane (644 mmol) in 50 milliliters of 1,1,2-trichlorotri-fluoroethane was added to a mixture of 0.390 gram of 1,4-butanediol (4.33 mmol), 1.55 grams of boron trifluoride tetrahydrofuranate (11.1 mmol), and 100 milliliters of methylene chloride at 18°C. The mixture was stirred at 18°C. for 3 hours, quenched with water, and precipitated into methanol to give, after drying at 85°C./2 mm-Hg for 16 hours, 186 grams of a clear, colorless oil, corresponding to 85 percent yield. NMR analysis revealed that this material was a 22:78 random copolymer of the above two monomers.

The polymer analyses were: DSC, T_g= -42°C.; GPC (THF, polystyrene standard) Number Average Molecular weight was 15,660; Weight Average Molecular Weight was 30,640; Polydispersity was 1.96; Number Average Molecular Weight by ^1H NMR was 18,400; Functionality was 2; Inherent viscosity was 0.071; ^1H NMR ($CDCl_3$/Freon 113) δ 0.91 (s, $C\underline{H}_3$), 3.22 (m, backbone $-C\underline{H}_2$'S), 3.44 (s, $-C\underline{H}_2O$), 3.79 (q, J=8.8 Hz, $-C\underline{H}_2CF_3$) and 3.86 (t, J=13.5 Hz, $-C\underline{H}_2C_3F_7$); ^1H NMR $CDCl_3$/Freon 113/ Trifluoroacetic anhydride) δ 0.95 (s, $-C\underline{H}_3$), 3.23 (m, backbone $-C\underline{H}_2$'S), 3.46 (s,$-C\underline{H}_2O$), 3.77 (q, J=8.6 Hz, $C\underline{H}_2CF_3$), 3.87 (t, J=13.5 Hz, $-C\underline{H}_2C_3F_7$), and 4.31 (s, $C\underline{H}_2OCOCF_3$); ^{13}C NMR ($CDCl_3$/Freon 113) δ 17.3, 41.6, 41.8, 68.6 (t), 69.3 (q), 74.2, 75.6, and 75.9 (signals from carbons bearing fluorine are not included).

In a similar manner, random copolymers of above monomers in 50:50 and 75:25 ratios were also prepared. The copolymers were clear, colorless oils that were soluble in tetrahydrofuran, methylene chloride and

1,1,2-trichlorotrifluoroethane (Freon 113).

EXAMPLE 15

POLYMERIZATION OF 3-(3,3,4,4,5,5,6,6,7,7,8,8,8-TRIDECAFLUOROOCTYLOXYMETHYL)-3-METHYLOXETANE

In a manner similar to that described in Example VII, a solution of 10 grams of 3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxymethyl)-3-methyloxetane (22.3 mmol) in three milliliters of Freon 113 was added dropwise to a mixture of 109 milligrams of boron trifluoride tetrahydrofuranate (0.78 mmol) and 35 milligrams of 1,4-butanediol (0.39 mmol) in methylene chloride at 10°C. The mixture was stirred at room temperature for 24 hours, quenched with water, and precipitated in methanol to give, after drying at 80°c/2 mm-Hg for 16 hours, 8.3 gram of poly 3-(3,3,4,4,5,5,-6,6,7,7,8,8,8-tridecafluorooctyl-oxymethyl)-3-methyloxetane, a clear colorless oil. The polymer analyses were: Inherent viscosity (THF/30°C.) was 0.067 dL/g; GPC: M_n = 5,340, M_w = 6,620, Poly Dispersity = 1.24; DSC, Tg = -38°C.; ^{1}H NMR ($CDCl_3$/Freon 113) δ 3.67 (t, 5.9 Hz, 2 H), 3.31 (s, 2 H), 3.21 (m, 4 H), 2.35 (m, 2 H), and 0.93 (s, 3 H); ^{1}H NMR ($CDCl_3$/Freon 113) δ 0.95 (s, 3 H), 2.37 (br t, J=18.3 Hz, 2 H), 3.25 (m, 4 H), 3.35 (s, 2H), 3.71 (t, 6.0 Hz, 2 H), and 4.30 (AB, $-C\underline{H}_2OCOCF_3$); Number Average Molecular Weight based on ^{1}H NMR was 4,756; ^{13}C NMR ($CDCl_3$/Freon 113) δ 17.35, 31.75 (t) , 41.5, 63.4, 74.1 and 74.3.

EXAMPLE 16

COPOLYMERIZATION OF A MIXTURE OF 3,3,4,4,5,5,6,6,7,7,8,8,8-TRIDECAFLUOROOCTYLOXYMETHYL-, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-HEPTADECAFLUORODECYLOXYMETHYL-, AND 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-HENEICOSAFLUORODODECYLOXYMETHYL-3-METHYLOXETANE

In a manner similar to that described in Example 13, a solution of 30 grams of C8- (73%), C10- (24%), and C12-(3%) oxetane monomers (62 mmol) in 10 milliliters of Freon 113 was added dropwise to a mixture of 300 milligrams of boron

trifluoride tetrahydrofuranate (2.14 mmol) and 95 milligrams of 1,4- butanediol (1.05 mmol) in 30 milliliters of methylene chloride at 10°C. The mixture was stirred at room temperature for 24 hours, quenched with water, and precipitated in methanol to give, after drying at 80°C./2 mm-Hg for 16 hours, 24 grams of the title copolymer, corresponding to 80 percent yield. The copolymer was a colorless, viscous oil. The analysis of the copolymer was: Inherent viscosity = 0.075 dL/g; GPC: M_n = 6,639, M_w = 9,368, Poly Dispersity = 1.41; ^1H NMR ($CDCl_3$/Freon 113) δ 0.95 (s, 3 H), 2.37 (br t, J=18.3 Hz, 2 H), 3.25 (m, 4 H), 3.35 (s, 2H), 3.71 (t, 6.0 Hz, 2 H), and 4.30 (AB, $-C\underline{H}_2OCOCF_3$); Number Average Molecular Weight based on ^1H NMR was 5,021; ^{13}C NMR ($CDCl_3$/Freon 113) δ 17.35, 31.75 (t), 41.1, 41.5, 63.4, 74.1 and 74.3.

EXAMPLE 17

POLYMERIZATION OF 3,3-BIS(2,2,3,3,4,4,4-HEPTAFLUOROBUTOXYMETHYL)OXETANE

In a manner similar to that described in Example 13 , a solution of 252 grams of 3,3-bis(2,2,3,3,4,4,4-heptafluorobutoxymethyl)oxetane (523 mmol) in 75 milliliters of Freon 113 was added to a mixture of 1.05 grams of boron trifluoride tetrahydrofuranate (7.5 mmol) and 0.265 gram of 1,4-butanediol (2.93 mmol) in 178 milliliters of methylene chloride at 10°C. The mixture was stirred at room temperature for 48 hours at which time NMR analysis of an aliquot indicated 96 percent conversion. The reaction was quenched with water and the polymer was precipitated into methanol to give, after drying at 80°C./2 mm-Hg for 16 hours, 211 grams of poly 3,3-bis (2,2,3,3,4,4,4-heptafluorobutoxymethyl)oxetane, a colorless oil in 84 percent yield. GPC analysis of this oil revealed it was a mixture of 68% linear and 32% cyclic materials. The cyclic product was isolated and identified as the cyclic tetramer, a white waxy solid with a melting point 80°C.; ^1H NMR δ 3.87 (t, J=13.5 Hz, 4 H) , 3.54 (s, 4H), and 3.32 (S, 4H) (No end groups were observed on addition of trifluoroacetic anhydride); ^{13}C

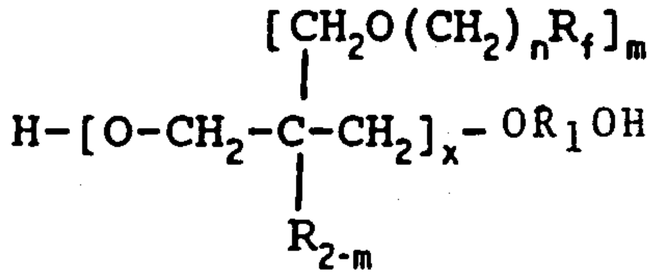
NMR δ 71.2, 68.6, 68.4 (t), and 46.2 (signals due to carbons bearing fluorine are not included).

The above oil was further purified by first dissolving the material in methylene chloride/Freon 113 (75:25 mixture), precipitating the polymer into a 10 fold excess of methanol, stirring the precipitated oil with tetrahydrofuran at room temperature for 2 days, and finally separating and drying the insoluble fraction at 85°C. at 2 mm-Hg for 16 hours. This yielded 128 grams of a clear, viscous oil, corresponding to 51% overall yield. The oil by GPC analysis was determined to be a mixture of 91% linear polymer and 9% cyclic tetramer. The polymer analyses were: DSC, Tg = -43°C gpc: M_n=5,526, M_w = 7,336, PD = 1.32; ^{1}H NMR ($CDCl_3$/Freon 113/TFAA) δ 3.39 (s, 4 H), 3.59 (s, 4 H), 3.87 (t, J=13.5 Hz, 4 H) and 4.40 (s, $-CH_2OCOCF_3$); Number Average Molecular Weight based on ^{1}H NMR = 5,200; ^{13}C NMR ($CDCl_3$/Freon 113) δ 46.4, 68.5 (t), 70.1 and 72.1 (signals from carbons bearing fluorines are not included).

The invention has been described with reference to the illustrated and presently preferred embodiment. It is not intended that the invention be unduly limited by this disclosure of the presently preferred embodiment. Instead, it is intended that the invention be defined, by the compounds, products and their equivalents, and the method steps and their equivalents, as set forth in the following claims:

CLAIMS:

1. A hydroxyterminated prepolymer having the structure:



wherein:

n is 1 to 5;

m is 1;

R is hydrogen or alkyl having from 1 to 4 carbons;

R_1 is alkylene or isoalkylene having 2 to 5 carbons;

R_f is linear or branched chain perfluorinated alkyl having from 1 to 20 carbons, or an oxa-perfluorinated polyether, having from 4 to about 60 carbons; and

x is 2 to about 250.

2. The hydroxyterminated prepolymer of claim 1 wherein said R_f is trifluoromethyl.

3. The hydroxyterminated prepolymer of claim 1 wherein said R_f is heptafluoropropyl.

4. The hydroxyterminated prepolymer of claim 1 wherein said R_f is pentadecafluoroheptyl.

5. The hydroxyterminated prepolymer of claim 1 wherein m is 1 and n is 1.

6. The hydroxyterminated prepolymer of claim 5 wherein said R_f is trifluoromethyl.

7. The hydroxyterminated prepolymer of claim 5 wherein said R_f is heptafluoropropyl.

8. The hydroxyterminated prepolymer of claim 5 wherein said R_f is pentadecafluoroheptyl.

9. The hydroxyterminated prepolymer of claim 1 wherein m is 1 and n is 2.

10. The hydroxyterminated prepolymer of claim 9 wherein said R_f is tridecafluorohexyl.

11. The hydroxyterminated prepolymer of claim 9 wherein said R_f is heptadecafluorooctyl.

12. The hydroxyterminated prepolymer of claim 9 wherein said R_f is henicosafluorodecyl.

13. A hydroxyterminated prepolymer having a molecular weight from 1,000 to about 30,000, and a polymer backbone resulting from the opening of the oxetane ring of oxetane monomers substituted at the 3 carbon position with one perfluorinated alkoxide group of the formula:

$$CH_2O(CH_2)_nR_f$$

wherein:

n is 1 or 2; and

R_f is linear or branched chain perfluorinated alkyl having from 1 to 20 carbons, or an oxa-perfluorinated polyether, having from 4 to about 60 carbons.

14. The hydroxyterminated prepolymer of claim 13 wherein n is 2.

15. The hydroxyterminated prepolymer of claim 14 wherein said R_f is tridecafluorohexyl.

16. The hydroxyterminated prepolymer of claim 14 wherein said R_f is heptadecafluorooctyl.

17. The hydroxyterminated prepolymer of claim 16 wherein said polymer backbone is a copolymer of two or three oxetane monomers having different R_f groups.

18. The hydroxyterminated prepolymer of claim 14 wherein said R_f is henicosafluorodecyl.

19. The hydroxyterminated prepolymer of claim 18 wherein said polymer backbone is a copolymer of two or three oxetane monomers having different R_f groups.

20. The hydroxyterminated prepolymer of claim 13 wherein n is 1.

21. The hydroxyterminated prepolymer of claim 20 wherein R_f is trifluoromethyl.

22. The hydroxyterminated prepolymer of claim 21 wherein said polymer backbone is a copolymer of two or three oxetane monomers having different R_f groups.

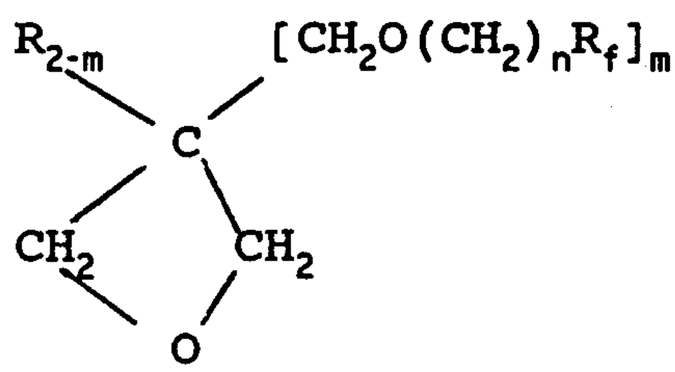
23. The hydroxyterminated prepolymer of claim 20 wherein R_f is heptafluoropropyl.

24. The hydroxyterminated prepolymer of claim 23 wherein said polymer backbone is a copolymer of two or three oxetane monomers having different R_f groups.

25. The hydroxyterminated prepolymer of claim 20 wherein R_f is pentadecafluoroheptyl.

26. The hydroxyterminated prepolymer of claim 25 wherein said polymer backbone is a copolymer of two or three oxetane monomers having different R_f groups.

27. A perfluorinated alkoxy oxetane monomer having the formula:



wherein:

n is 1 to 5;

m is 1;

R is hydrogen or alkyl having from 1 to 4 carbons; and

R_f is linear or branched chain perfluorinated alkyl having from 1 to 20 carbons, or an oxa-perfluorinated polyether, having from 4 to about 60 carbons.

28. The perfluorianted alkoxy oxetane monomer of claim 27 wherein R_f is perfluoroalkyl.

29. The perfluorinated alkoxy oxetane monomer of claim 28 wherein said R_f is trifluoromethyl.

30. The perfluorinated alkoxy oxetane monomer of claim 28 wherein said R_f is heptafluoropropyl.

31. The perfluorinated alkoxy oxetane monomer of claim 28 wherein said R_f is pentadecafluoroheptyl.

32. The perfluorinated alkoxy oxetane monomer of claim 28 wherein m is 1 and n is 1.

33. The perfluorinated alkoxy oxetane monomer of claim 32 wherein said R_f is trifluoromethyl.

34. The perfluorinated alkoxy oxetane monomer of claim 32 wherein said R_f is heptafluoropropyl.

35. The perfluorinated alkoxy oxetane monomer of claim 32 wherein said R_f is pentadecafluoroheptyl.

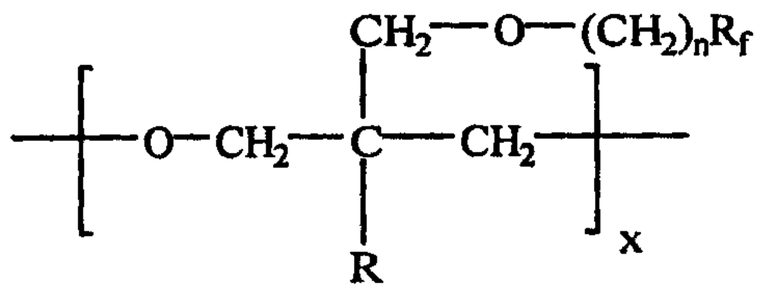
36. The perfluorinated alkoxy oxetane monomer of claim 28 wherein m is 1 and n is 2.

37. The perfluorinated alkoxy oxetane monomer of claim 36 wherein said R_f is tridecafluorohexyl.

38. The perfluorinated alkoxy oxetane monomer of claim 36 wherein said R_f is heptadecafluorooctyl.

39. The perfluorinated alkoxy oxetane monomer of claim 36 wherein said R_f is henicosafluorodecyl.

40. A hydroxyterminated prepolymer comprising a monomeric repeat unit represented by the formula:

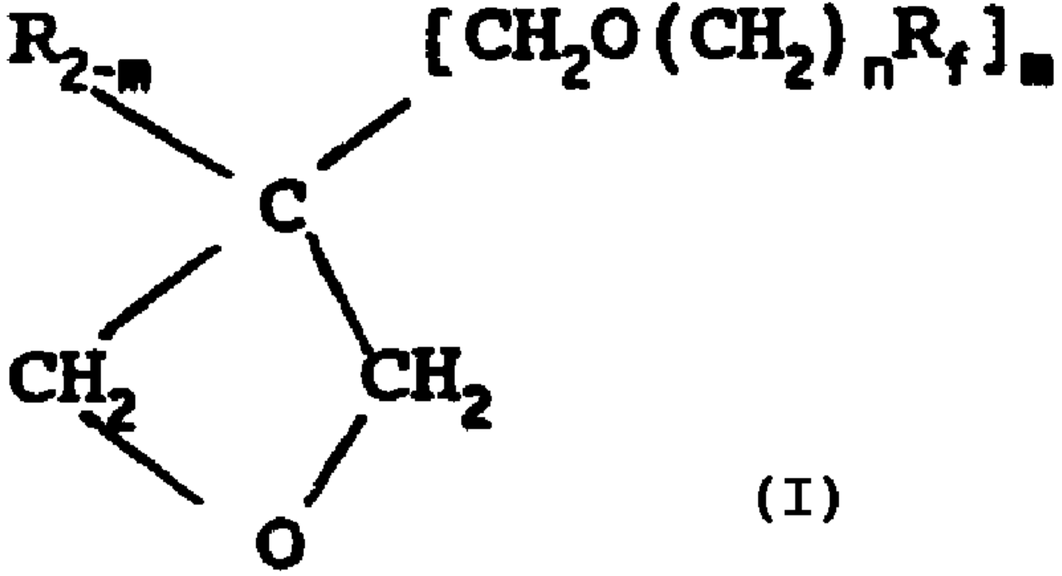


wherein:

n is 1 to 5;

R is hydrogen or alkyl having from 1 to 4 carbons;

R_f is linear or branched perfluorinated alkyls having from 1 to about 20 carbon atoms, or oxa-perfluorinated polyethers, having from 4 to about 60 carbons; and x is 2 to about 250.



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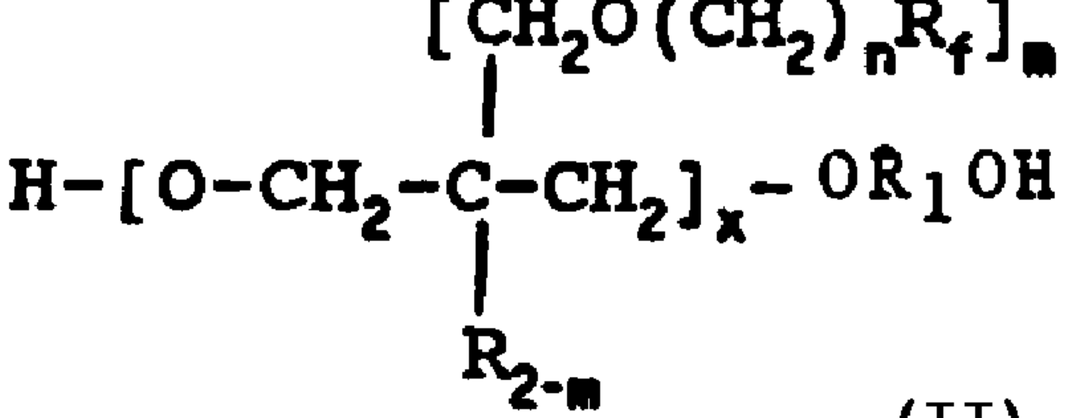

(II)